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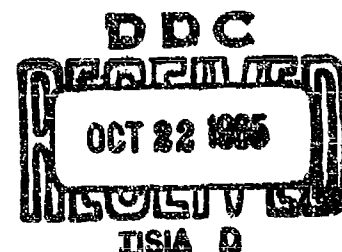
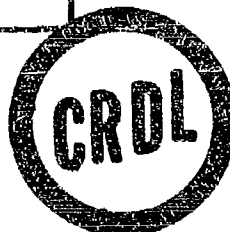
**CRDLR 3295**

**Perspectives in Detection  
Volume I**

by

**Edward J. Pozniomek**

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**EDGEWOOD ARSENAL, MARYLAND 21010**

CRDLR 3295

PERSPECTIVES IN DETECTION

Volume I

by

Edward J. Poziomek

Defensive Research Division  
Directorate of Defensive Systems

August 1965

US Army Edgewood Arsenal  
CHEMICAL RESEARCH AND DEVELOPMENT LABORATORIES  
Edgewood Arsenal, Maryland 21010

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## FOREWORD

This work was conducted under Project 1A014501A91A, In-House Laboratory Independent Research Program (U). The work was started in February 1964 and completed in February 1965.

## Acknowledgment

The author wishes to acknowledge the help of Miss Pat Lehmen, an Edgewood High School senior, in various tedious tasks such as abstract assimilation, index preparation, etc.

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## Disposition

When this report has served its purpose, DESTROY it.

## DIGEST

This publication is intended for research workers in detection and includes a current survey of 15 topics. The subjects are: catalytic and chain reactions, chromatography, class tests, films, fluorescence-chemiluminescence, general considerations, kinetics, metal ions, olfaction, photochemistry, reaction mechanisms, reagents, general reviews, solids-surfaces, and theoretical considerations.

The objective is to stimulate thinking on the solution of various detection problems by providing a convenient source of references from the current literature.

The report consists of a general discussion, an annotated bibliography, and a subject index to the bibliography.

Current literature contains much information that can be used as background in attempting to solve detection problems. Detailed analysis is not the purpose of this report and is, instead, left to individual users.

A noticeable trend worth mentioning is the increasing use of free radicals as reagents, intermediates, or products in analytical reactions. Chiefly because of their rapid rates, free-radical reactions should be more closely examined for detection applications.

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# PERSPECTIVES IN DETECTION

## Volume I

### I. INTRODUCTION.

This publication is intended for research workers in detection. Its purpose is to stimulate thinking on the solution of various detection problems by providing a convenient source of references from the contemporary literature.

Fifteen topics were chosen on the basis of general interests of the author. The annotated bibliography was drawn mostly from the 1963-1964 physical-chemistry and organic-chemistry sections of Chemical Abstracts. The references are listed alphabetically in each section by author. There is also a subject index to the bibliography. The topics were not reviewed completely. Instead, references were selected with the purpose of allowing ideas to generate along certain lines.

The discussion emphasizes specific interests of the author and deals with new technology, new applications of known principles, reaction mechanisms, and ways of achieving high sensitivities.

Inclusion of "Volume I" in the title provides for possible extension to a series should the response to this volume justify such action.

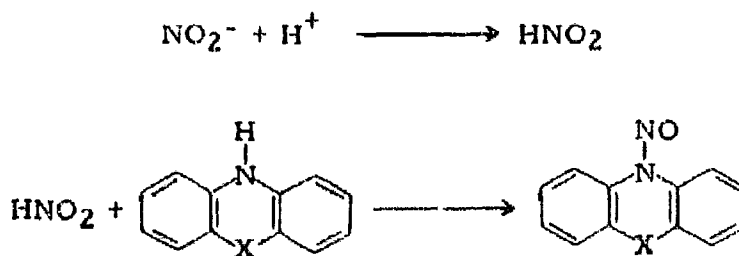
### II. DISCUSSION.

#### A. Catalytic and Chain Reactions.

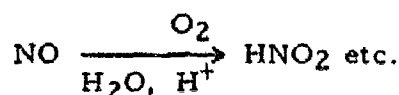
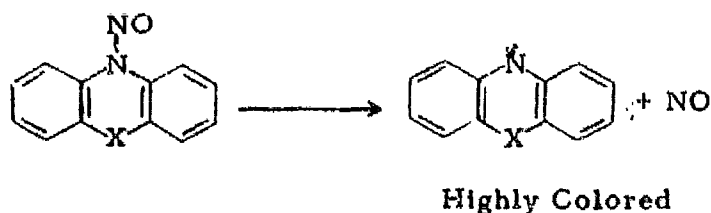
The need for learning more about catalytic and chain-type mechanisms, especially at low reagent concentrations, was emphasized recently in connection with a theoretical analysis of existing problems in the microchemical detection of toxic chemical agents.<sup>1</sup> Numerous catalytic reactions have been reported, and recent examples are cited in the annotated bibliography.

Two of the more promising areas, from a detection viewpoint, involve metal-ion catalysis and free-radical reactions. Metal-ion-catalyzed reactions are extremely sensitive and are discussed in a separate section. Relatively little has been done in applying free-radical reactions to detection problems, even though the reactions are very rapid.

Methods for determining nitrite ion and its precursors by measuring visible absorption of free-radical chromogens are claimed by Sawicki and co-workers<sup>2</sup> to be more sensitive than any previously described in the literature. A probable mechanism through chain reactions is shown in scheme I.



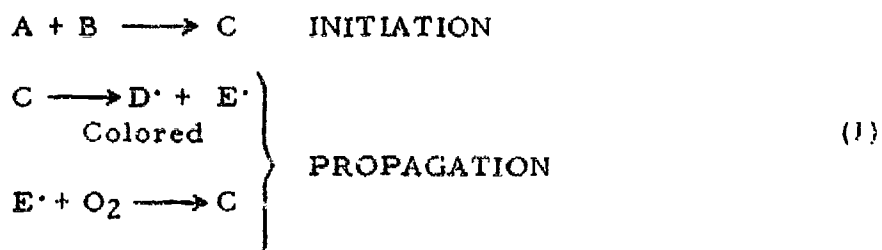
where X = S, Se, O



SCHEME I

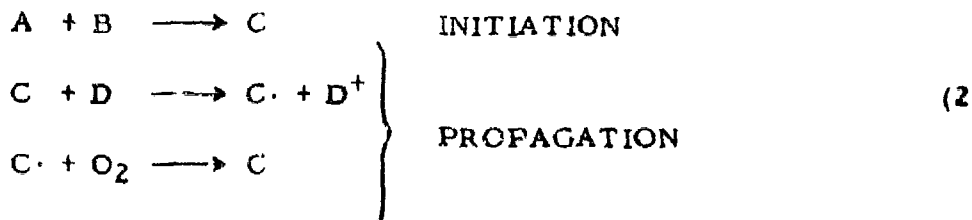
#### DETECTION OF NITRITE ION THROUGH A CHAIN-REACTION MECHANISM

Scheme I may be represented more simply as:

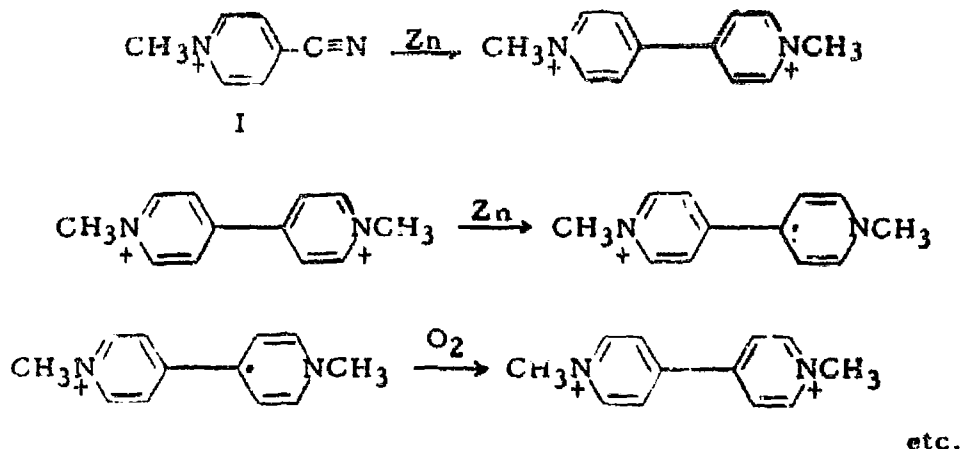


in which detection is based on observing or measuring the color of  $\text{D}^\bullet$ , a free radical more stable to oxidation than  $\text{E}^\bullet$ .

Of course, other variations of oxidation-reduction chain cycles may be written as follows:



Detection would be based on observing or measuring the disappearance of D or the appearance of  $D^+$ . The problem is to apply such schemes to detection. Known pyridinyl free-radical reactions<sup>3</sup> could be used to apply reaction cycle 2 to the detection of 1-methyl-4-cyanopyridinium salts (I) or their precursors (scheme II). Other oxidizing agents could be used instead of oxygen. Preliminary results on testing scheme II for use in detection are very encouraging.\*



SCHEME II

## DETECTION OF 1-METHYL-4-CYANOPYRIDINIUM SALTS THROUGH A CHAIN-REACTION MECHANISM

### B. Chromatography.

The potential of chromatography for analytical use continues to grow. An electron-capture detector in conjunction with a chromatographic column has been used to detect as low as  $10^{-12}$  M of organic iodides present

\* Hasselberger, F. Unpublished results.

in a hydrocarbon.<sup>4</sup> The combination of a gas-chromatographic column and an electron-capture detector will also detect and measure concentrations of phosgene on the order of 1,000 times less than those of physiological interest.<sup>5</sup>

For handling high-speed analyses, gas-solid chromatography theoretically promises approximately  $10^7$  plates/sec.<sup>6</sup> Despite certain limitations, gas-solid chromatography should be especially useful in measuring surface kinetics.

A major advance in recent years has been the acceptance of thin-layer chromatography as a very versatile analytical tool in the laboratory. Generally, thin-layer methods have been found to give separations superior to the paper method. Recovery of samples for quantitative analysis is easier. Even simple measurement of the length of each sample zone can give reasonably good quantitative analysis if the thin layer has uniform narrow width.<sup>7</sup>

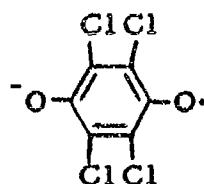
Advantage has been taken of the greater sensitivity and shorter running time of thin-layer chromatography over paper chromatography to separate mixtures of quaternary ammonium compounds at levels as low as 0.5 to 1.0  $\mu\text{g}$ .<sup>8</sup>

Rapid, thin-layer chromatographic methods for the identification of some common flavor esters by both their reaction with certain specific spray reagents and their  $R_f$  values have been described.<sup>9</sup>

A variety of procedures has been developed for revealing and identifying spots. A recent book on thin-layer chromatography describes the many techniques.<sup>10</sup>

### C. Class Tests.

The usefulness of tetracyanoethylene as a general reagent for the detection of a variety of classes of organic compounds is cited in the fluorescence-chemiluminescence section. Another useful reagent is chloranil. Molecular complexes of aromatic amines with chloranil in chloroform have characteristic charge-transfer absorption bands in the visible region.<sup>11, 12</sup> Substitution of chlorine usually occurs in the interaction of chloranil with aliphatic amines; however, solutions of chloranil in pure triethylamine yield a product that appears to be a salt, the anion of which is the free-radical semiquinone ion (II) derived from chloranil.



## II

Chemical reactions and instrumental methods for the identification of the following classes of compounds have been reviewed recently: hydroxy, carboxylic acids, carbonyl, amines, amino acids, N-oxides, organosulfur, alkoxy, and hydrocarbons. The author emphasizes that a combination of qualitative and quantitative methods is necessary for obtaining a final identification.<sup>13</sup>

A systematic analysis by using test papers has been developed for cations. The cations are first separated into five groups with sodium hydroxide and diethyldithiocarbamate. Each cation is then identified without further separation using specific test papers. Most of the test papers are still usable after 1 yr. The limits of identification (parts per million) are: (1)  $\text{Cd}^{++}$ ; (2)  $\text{Ni}^{++}$ ; (5)  $\text{Co}^{++}$ ; (10)  $\text{Cu}^{++}$ ; (25)  $\text{Al}^{+3}$ ,  $\text{Sb}^{+3}$ ,  $\text{Fe}^{+3}$ , and  $\text{NH}_4^+$ ; (50)  $\text{As}^{+3}$ ,  $\text{Zn}^{++}$ ,  $\text{Bi}^{+3}$ ,  $\text{Mn}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ; (100)  $\text{Pb}^{++}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{++}$ ,  $\text{Cr}^{+3}$ ; and (250)  $\text{Ca}^{++}$ .<sup>14</sup>

Jimeno<sup>15</sup> summarized methods for direct detection of the following anions in solution:  $\text{CO}_3^{--}$ ,  $\text{SiO}_3^{--}$ ,  $\text{PO}_4^{-3}$ ,  $\text{F}^-$ ,  $\text{AsO}_4^{-3}$ ,  $\text{AsO}_2^-$ ,  $\text{CrO}_4^{--}$ ,  $\text{Fe}(\text{CN})_6^{-3}$ ,  $\text{Fe}(\text{CN})_6^{-4}$ ,  $\text{S}^{--}$ ,  $\text{SO}_3^{--}$ ,  $\text{S}_2\text{O}_3^{--}$ ,  $\text{SCN}^-$ ,  $\text{CN}^-$ ,  $\text{C}_2\text{O}_4^{--}$ , borate, tartrate, acetate,  $\text{SO}_4^{--}$ ,  $\text{NO}_2^-$ ,  $\text{IO}_3^-$ ,  $\text{I}^-$ ,  $\text{BrO}_3^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{ClO}_3^-$ , and  $\text{NO}_3^-$ .

A reported spot test for chlorine in inorganic and organic compounds is based on permanganate oxidation in acid, heating, and then forming a blue-green color on diphenylamine paper held over the test solution.<sup>16</sup>

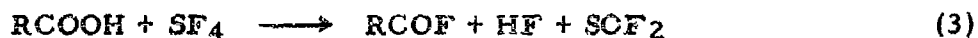
It was indicated that 0.001 to 10 ppm of iodide can be detected on the basis of its catalytic effect on the fading of the ferric thiocyanate color in dilute nitric acid containing a small amount of nitrite ion. Iodine, iodate, and periodate can be detected by the same procedure.<sup>17</sup>

A versatile reagent for the detection of carbonyl compounds is 3-methyl-2-benzothiazolone hydrazone.<sup>18</sup> Aldehydes react in the presence of ferric chloride to form a blue cationic dye in acidic media. A recent modification is the addition of sulfamic acid, which gives in the oxidizing step a solution free of turbidity.<sup>19</sup> It is claimed that aliphatic aldehydes may be analyzed in the parts-per-billion range in ambient air.

A method for the determination of organic peracids and hydrogen peroxide in mixtures is known.<sup>20</sup> Analysis is based on rapid reaction of peracids with neutral potassium iodide and on the formation of a stable complex between hydrogen peroxide and titanyl ions. The complex is decomposed with sodium fluoride, and the resulting reaction with iodide is accelerated with molybdic acid.

Pentacyanonitrosferrate and zinc chloride have been used to detect 1 to 2  $\mu$ g of mercapto compounds at pH 5 to 8.<sup>21</sup> N-Nitroso compounds have been detected by diphenylamine-palladium (II) chloride (blue to red-violet, 0.5  $\gamma$  to 1  $\gamma$ ) and sulfanilic acid-1-naphthylamine reagent (green, blue, to red-violet, 0.2  $\gamma$  to 0.5  $\gamma$ ) under ultraviolet light. Quinoid and nitro compounds interfere with the diphenylamine reagent.

Carboxyl groups have been determined in the presence of carbonyl groups by using sulfur tetrafluoride and measuring infrared absorption of acid fluoride [equation (3)].<sup>22</sup>



Free radicals are present in colored mixtures produced by the Marquis test (solution of formaldehyde in concentrated sulfuric acid) for alkaloids. Free radicals were also found in colored mixtures produced by other tests in which sulfuric acid is the reaction solvent. In most cases, the observed electron-spin-resonance (esr) spectra exhibited a time dependency and indicated mixtures of free radicals.<sup>23</sup>

The use of aluminum chloride for the analysis of classes of compounds and functional groups has been investigated in detail by Talsky.<sup>24, 25</sup> A numerical scale was proposed on the basis of the colors formed in a variety of solvents so that a compound can be identified by the sum of these numbers.<sup>25</sup> The classes of compounds included hydrocarbons, halogen compounds, alcohols,

aldehydes, ketones, nitro compounds, nitriles, amines, phenols, carboxylic acids, anhydrides, acyl halides, amides, anilides, esters, ethers, sulfonic acids, sulfones, sulfides, and heterocycles.

Talsky's success in using a single nonspecific reagent with a number of solvents to identify various chemicals is evidence for the potential of a "rouechimio" approach in attempting to develop simple identification schemes. Rouechimio is a term coined to describe the use of a combination of colors formed from relatively few nonspecific reagents for the specific and rapid identification of classes of compounds and functional groups.

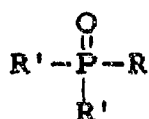
#### D. Films.

By far the simplest detection devices would be film badges that change on exposure to chemical agents in a striking manner (e. g., formation of color, rupture, formation of chemiluminescence, etc.). There is, however, only a limited amount of reported work in the properties of films, and there are no references on the use of films for detection purposes.

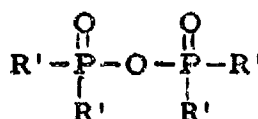
Photographic technology provides the greatest numbers of examples of what can be achieved. 26-29 Nondiffusing reducing agents are easily incorporated in multilayer films. 26 A 0.075- to 6.25-mm coating of an unsaturated compound is polymerizable under the influence of a photoinitiator liberating free radicals. 28 Kinetics of color development in a multilayer film badge have been studied. 27 Photoexposed silver layers have been subjected to diethylamine vapor as an alkali, N,N-diethylhydroxylamine as a developer, and hydrogen sulfide as a fixer. 30

Certain photographic film processes may be adaptable to detection. For example, a known photopolymerizable film consists of 30 parts of triethylene glycol diacrylate, 67 parts of cellulose acetate succinate (as binder), 0.13 part of 2-ethylanthraquinone (initiator), and 0.13 part of p-methoxyphenol (thermal polymerization inhibitor). 28 In a detection application, the initiator could be substituted by a reagent that is known to give free radicals on reaction with chemical agents. Detection would be based on visually observing polymerization or measuring a film property.

Photoconductivity has been claimed when zinc oxide films were exposed to vapors of an organophosphorus compound of types III or IV. 31



III



IV

where

R = H, halogen atom, metal atom,  $\text{NH}_4^+$  or an onium group, or OH

R' = halogen atom, OH, alkyl, aryl, or alkoxy

Specific sensitivity details were not available, but this and other known photoconductive films may be found useful in detection.

Vitrified, cholesteric, single-crystal films with a solid consistency have been obtained from thin layers of cholesteryl cinnamate. A vitrified texture resulted that remained stable and showed the rainbow colors typical for a cholesteric structure.<sup>32</sup> More attention should be given to finding practical uses of the optical, electrical, and magnetic properties of liquid crystals.

#### E. Fluorescence-Chemiluminescence.

Fluorescence methods of detection are attractive because of their greater sensitivity in comparison to ultraviolet and infrared methods and are, in some cases, very valuable when only trace amounts of materials are available for investigation. Spectrofluorometry is claimed to be 1,000 times more sensitive than spectrophotometric methods in monitoring the reaction of carbonyls with 2-diphenylacetyl-1,3-indanedione-1-hydrazone. Completeness of reaction was confirmed in  $5.0 \times 10^{-4}$  to  $5.0 \times 10^{-7}$  M solutions.<sup>33</sup>

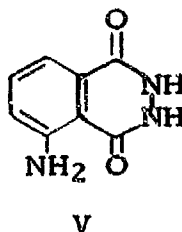
Nonfluorescent compounds such as anthraquinone, p-hydroxyacetophenone, and p-nitroaniline can be more readily detected and determined in mixtures by phosphorimetry. As little as 0.1 mug of anthrone has been detected with this technique.<sup>34</sup>

Tetracyanoethylene (TCNE) exposed to benzene vapor fluoresces light yellow under ultraviolet light (366 mμ).<sup>35</sup> Bright fluorescent flashes were also observed when toluene and xylene solutions of TCNE were allowed

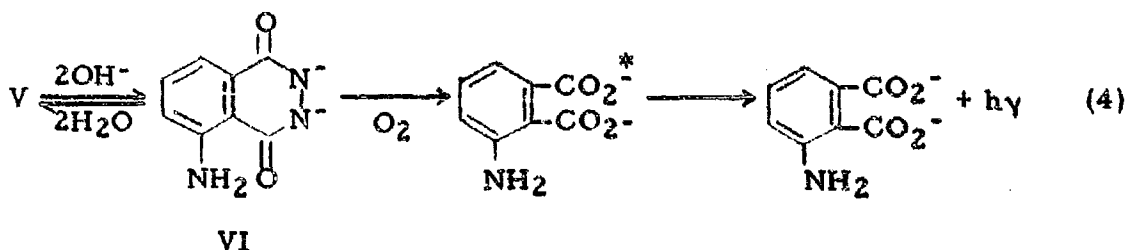


to evaporate on filter paper. TCNE is already a useful reagent in applications such as the detection of nitrogen compounds in petroleum,<sup>36</sup> development of paper chromatograms,<sup>37</sup> colorimetric determination of anthracene,<sup>38</sup> and the titrimetric estimation of dienes by the Diels-Alder reaction.<sup>39</sup> The general observations on fluorescence indicate the potential of rendering TCNE even more useful as an analytical reagent.

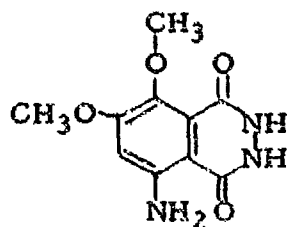
Many chemiluminescent reactions are known, but little is known about the chemistry involved. Luminol (5-amino-2,3-dihydro-1,4-phthalazine-dione, V) is one of the most efficient and probably the best known of the chemiluminescent compounds. In the absence of oxygen, basic solutions of Luminol are stable indefinitely. Light is produced when basic aqueous solutions containing oxygen are treated with an oxidizing agent, and this has been made the basis of detection methods.<sup>40</sup> The light emitted in the chemiluminescence of Luminol (about 350 to 600 mμ) has an energy equivalence of about 50 to 80 kcal/mole.



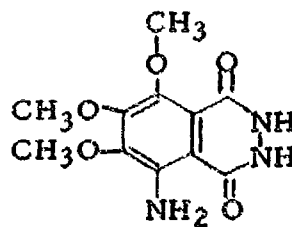
White and coworkers<sup>41, 42</sup> showed that the main steps in the chemiluminescence of Luminol are the reaction of the dinegative ion of Luminol (VI) with oxygen to eventually yield an excited singlet state of the aminophthalate ion and the emission of light by this species [equation (4)].



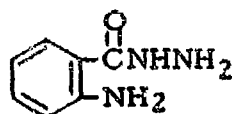
Electron-supplying substituents increase the efficiency of emission in both chemiluminescence and fluorescence.<sup>43, 44</sup> Thus, compounds VII and VIII have been found to be more efficient in light production than Luminol.<sup>42</sup> The analogous o- and m-aminobenzhydrazides IX and X chemiluminesce, but less efficiently than Luminol. The o- and m-aminobenzoates XI and XII are fluorescent. The corresponding para derivatives are neither chemiluminescent nor fluorescent in the visible region.



VII



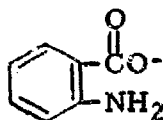
VIII



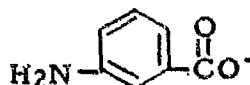
IX



X



XI



XII

Chandross and Sonntag<sup>45</sup> have discovered a new type of chemiluminescent reaction that promises to be one of the most general types known. It involves electron abstraction from an aromatic hydrocarbon-radical anion by a suitable oxidizing agent. Bright chemiluminescence accompanies the reaction of potassium 9,10-diphenylanthracene with various electron acceptors, such as chlorine, benzoyl peroxide, oxalyl chloride, mercuric chloride, and aluminum chloride. The chemiluminescent process is not limited to hydrocarbon ions, and it is expected that radical anions derived from various fluorescent species will exhibit this behavior.

It is important to point out in this discussion of fluorescence and chemiluminescence that a reaction is not likely to generate a product in an excited electronic state simply because it provides sufficient energy to do so. In reactions that involve bond formation or cleavage or both, the energy will not likely be liberated as fast as it is in a reaction involving only the transfer of an electron. The energy is more likely to be liberated relatively slowly and absorbed as bond vibrations in several molecules as the transition state is traversed.<sup>45</sup>

Observed effects of solvent, pH, concentration, and temperature on fluorescence spectra of aromatic compounds in dilute solution have been reviewed in detail.<sup>46</sup>

#### F. General.

This section describes existing technology and new techniques that may be useful in certain detection problems.

Manual and recording microspectrophotometers have been constructed that, in a single sweep, will give ultraviolet, visible, and near-infrared absorption spectra for specimen areas as small as 2 sq  $\mu$ .<sup>47</sup> Absorption spectra of the chloroplast of plant cells, the retina of the visual cells of the eye, and the red blood cell have been obtained.

Various microcells have been described for measuring infrared-absorption spectra. One cell is designed to contain a few microliters of volatile liquids and a few tenths of a microliter of nonvolatile liquids collected in capillary tubes from gas-chromatographic columns.<sup>48</sup> Others are made of polyethylene and will hold as little as 3  $\mu$ l of liquid or 3 mg or solid.<sup>49</sup>

Nuclear-magnetic-resonance integration has been applied to the determination of molecular weight. This involves comparison of the integrated intensities of an added standard and of a recognizable peak or group of peaks of the unknown in a solution containing known weights of standard and unknown.<sup>50</sup>

An automatic sampling mechanism has been described that, in conjunction with a spectrophotometer, can periodically collect gas samples from 10 separate atmospheres and obtain a record of the ammonia concentration in each. A mercury pump is used to draw samples consecutively into a

10-cm silica cell, and the absorbance at 204.3  $\mu$  is recorded. The samples are then returned to the atmosphere. The method is sensitive to 10 ppm.<sup>51</sup>

An instrument has been developed that will detect any vapor that can be treated in some manner to form particles in the order of tenths of a micron or less.<sup>52</sup> Sensitivities in the parts-per-million to parts-per-billion range have been achieved for acids, ammonia, amines, nickel carbonyl, tetraethyllead, and some halogenated hydrocarbons through application of gaseous conduction phenomena in an ionization chamber.

Very small amounts of materials ( $10^{-6}$  to  $10^{-9}$  gm) were found to be sufficient for recognition of products of mechanochemical microreactions brought about by pulverizing, grinding, scratching, or pressing solid materials. Reactions are described for detection of Fe, Co, Ni, W, Mo, or Ag.<sup>53</sup>

Glass tubing coated on the inside with an indicator was found to be more superior than indicator paper for testing pH.<sup>54</sup> The use of this technique is described with Methyl Violet.

Encapsulation is a technique that may be used for storing solvents or reagents and may simplify the design of detection devices. One of the problems in the existing technology, however, is encapsulation of water or aqueous solutions. Two patents appeared recently on water encapsulation.<sup>55, 56</sup> Microcapsules were prepared with polystyrene or vinylidene chloride-acrylonitrile copolymer coatings. Another potential mechanism of supplying water for reactions requiring it is acid-base neutralization. Development of Polacolor films is initiated by rupturing pods containing a viscous solution of alkaline activator.<sup>57</sup> Water is generated by neutralization of alkali and diffuses through the dye-image layer. Perhaps a similar technique could be worked out for film-detection reactions where water is required as a reactant.

#### G. Kinetics.

Theories of kinetics, mathematical and experimental details, and calculation of energies are all of great importance in a variety of considerations applicable to detection. Kinetics and Mechanisms by Frost and Pearson<sup>58</sup> is a work that shows the intimate relationship between kinetics and reaction mechanisms.

Basic to a design of new concepts in detection reactions is a better understanding of nucleation rates, kinetics of particle growth, diffusion kinetics of reactions, kinetics of reactions at very low reagent concentrations, and kinetics of chain reactions. There are no simple rules, and new ideas need to be evaluated individually.

#### H. Metal Ions.

Of the reported detection and catalytic reactions, the most sensitive, in general, are those involving metal ions. This is true in contemporary as well as older literature. Typical examples from the current literature follow.

Copper ions at a concentration of 0.01  $\mu\text{g/ml}$  have been detected by a catalytic oxidation of an ammoniacal solution of potassium guaiacolsulfonate.<sup>59</sup> Ethylenediaminetetraacetic acid has been used for qualitative detection of a variety of metal ions with sensitivities as low as 10 ppm.<sup>60</sup> Parts per billion of iron have been determined by a fluorescence extinction method based on the interference of iron in the fluorometric determination of Al with Pontachrome Blue Black.<sup>61</sup> (It was noted that fluoride and phosphate ion interfere seriously.) The catalytic activity of  $10^{-11}$  gm of cupric ion on the oxidation of indigo carmine by  $\text{H}_2\text{O}_2$  was studied.<sup>62</sup> The decomposition rate of hydrogen peroxide was found to be influenced by  $10^{-11}$  gm of  $\text{Ni}^{++}$  with cobaltous carbonate as the carrier substance.<sup>63</sup> As little as 1  $\mu\text{g}$  of cupric ion was visually detected by concentrating the colored cupric-amine complexes on montmorillonite.<sup>64</sup>

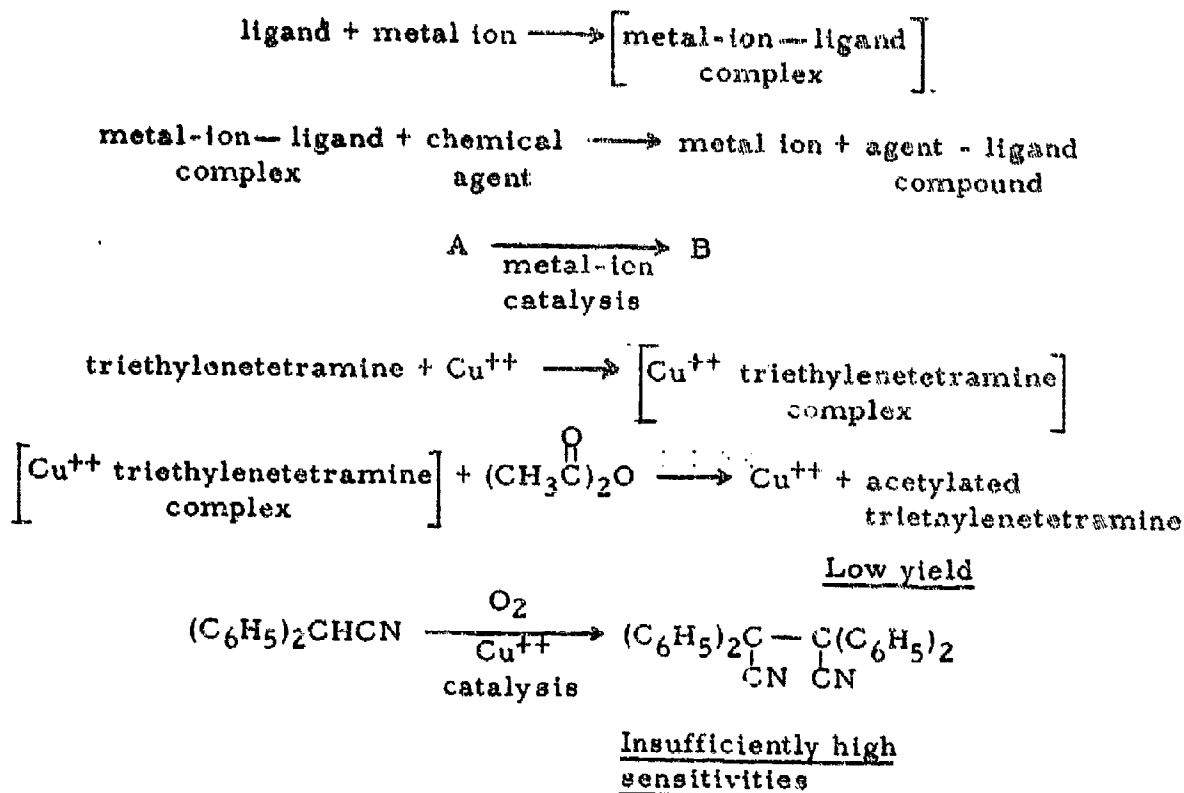
Metal ions have been used in a variety of catalytic applications. For example, cupric ion-amine complexes were selected as models of catalase activity.<sup>65</sup> Ions of alkali metals, alkaline-earth metals, and certain bivalent ions of the transition elements were found to accelerate the first-order hydrolysis rates of disulfates.<sup>66</sup>

Copper-bipyridyl chelates were shown to be excellent catalysts for the chemiluminescence of Luminol.<sup>67</sup> Also, the catalytic action of various metal salts in the oxidation of primary aromatic amines with peracetic acid has been elucidated.<sup>68</sup>

A variety of reactions other than oxidation-reduction types is known to be catalyzed by metal ions and is discussed in detail by Hay.<sup>69</sup>

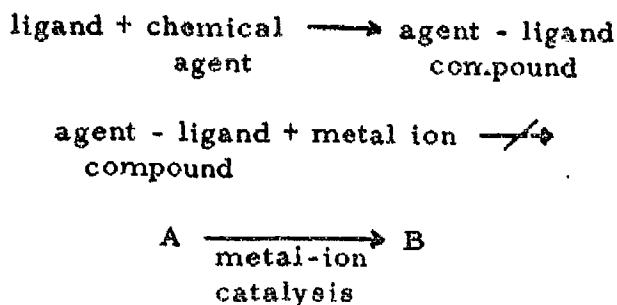
In view of the many potential uses of metal ions, it is very attractive to design schemes in which chemical agents are detected by the release of a catalytically effective metal ion. Such schemes have been tried by Sosnovsky (scheme III).<sup>70</sup> Insufficiently high sensitivities were obtained. On the other

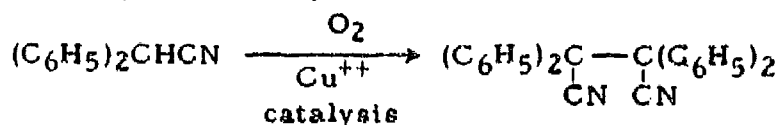
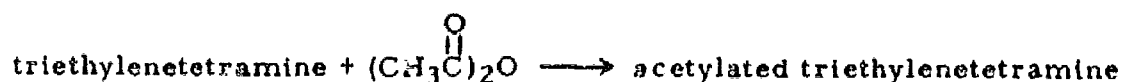
hand, 60  $\mu\text{g}$  of acetic anhydride in 10 ml were detected if the free ligand was allowed to react first with the acylating agent. On acylation, the amine becomes a far weaker complexing agent (scheme IV).



### SCHEME III

#### DETECTION REACTIONS CATALYZED BY THE RELEASE OF METAL ION





$\text{O}$   
 $\parallel$   
 50  $\mu\text{g}$  of  $(\text{CH}_3\text{C})_2\text{O}$  in 10 ml  
detectable by appearance of  
precipitate

#### SCHEME IV

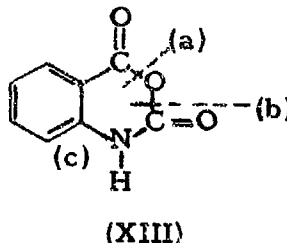
### DETECTION REACTIONS BASED ON THE INHIBITION OF METAL-ION COMPLEXATION

#### I. Olfaction.

Olfaction should be regarded as a method of measurement that can be rapid and inexpensive, often reasonably precise, applicable to very small quantities or concentrations of matter, and can lead to high levels of confidence that gross errors have not been made.<sup>71</sup> Published work on odor and physical properties, odor and chemical constitution, threshold concentrations, and olfaction mechanism was tabulated and discussed by Mosher,<sup>72</sup> with a view towards using olfaction as a detection method. The sensitivity of olfactory sensing methods merits recognition and serious attempts at application for detection.

It is very difficult to design a scheme of detection reactions based on odor perception. On the basis of reported human thresholds, certain alcohols, acids, amines, aldehydes, ketones, esters, isocyanides, or thiols are detectable in low enough concentrations to be considered as products in the detection reaction. Of course, the design of one-step reactions in which one of the reactants is a material to be detected is a major problem. Simple reactions based on hydrolysis, neutralization, displacement, or esterification mechanisms can be written, but nonspecificity results.

An interesting proposal is the use of isatoic anhydride sulfur analogs as reagents in detection reactions based on olfactory sensing.<sup>72</sup> The exceptional potential of isatoic anhydride (XIII) arises from the ease with which it enters into condensation, displacement, and electrophilic substitution reactions.<sup>73</sup> The hetero ring is highly susceptible to cleavage at (a) or (b) and yet can be N-alkylated at (c) with little or no ring opening. The condensation of (I) with aqueous ammonia and primary and secondary amines generally occurs on contact at low to moderate temperatures to give a good yield of the corresponding anthranilamide and carbon dioxide. If sulfur were substituted for one or more oxygens in XIII, carbon oxysulfide or carbon disulfide should form instead. Detection would be based on sensing the characteristic pungent odor of the volatile sulfur compound.



#### J. Photochemistry.

A knowledge of how light affects a chemical or a chemical reaction may be important in solving stability and sensitivity problems in detection. Furthermore, photochemical mechanisms may provide leads to new types of detection reactions.

An excellent review of approaches to new photographic processes appeared recently<sup>74</sup> and dealt with systems based on catalysis, on the variation of dielectric constant of a phosphor under illumination, on the reduction of semiconductor oxides, and on the quenching of color centers. Existing photo and reproduction processes were classified according to a triggering step (formation of a latent image), an amplification step (addition of external energy to the system), and a "fixing" step to render a permanent image.

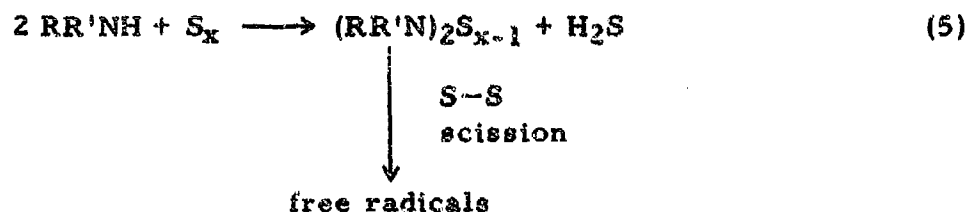
Characteristics of speed and sensitivity are of prime consideration in photographic processes, and new detection approaches may be guided by an examination of existing photomechanisms.. Accordingly, a study of the review by Robillard<sup>74</sup> on new approaches to photography cannot be overemphasized.



Du Pont has developed a new photographic process in which photosolubilization leads to a positive image rather than a negative image as in conventional photography.<sup>75</sup> Two basic steps, insolubilization and photosolubilization, are actually involved. Insolubilization presumably involves either adsorption or chemical binding of an organic compound on the surface of the silver halide. Photosolubilization occurs when a substance that contains the modified silver halide is exposed to light and then immersed in a solvent solution, forming a direct image in silver halide. Treatment of the unexposed emulsion with free bromine or chlorine has the same effect as does exposure to light. Insolubilization and solubilization processes should be examined in more detail for possible applications in the detection of chemical agents.

Light causes fluorescent dyes to bind to particles of zinc oxide or aluminum oxide.<sup>76</sup> Small amounts of p-phenylenediamine ( $10^{-6}$  M) retard the reaction. Conceivably, the phenomenon of dye adsorption could be applied to increasing visual-detection sensitivity. Alternatively, an inhibition of adsorption caused by traces of materials might be used to detect the interfering substances.

Electron-spin resonance has confirmed that free radicals were formed whenever elemental sulfur was dissolved in an amine to give a colored solution.<sup>77</sup> It has been suggested that the radicals are the result of homolytic scission of S-S bonds in N, N'-polythiobisamines, which are formed by step-wise nucleophilic attack on  $S_8$  rings by the amine [equation (5)].



Sulfur has also been used in the chemical sensitization of photographic emulsions.<sup>78-80</sup> There may be a possibility of combining the sensitizing phenomenon with equation (5) into a catalytic reaction for the detection of amines.

Horizons, Inc., has been doing work on free-radical photography processes since 1957.<sup>81-82</sup> Light decomposes one or more compounds and

produces free radicals that combine to form colored compounds. For example, N-vinyl carbazole and carbon tetrabromide, when exposed to ultraviolet light and then heated, form a brownish-black image. High sensitivity results from the fact that the light sets off a chain reaction. Detection reactions (those known to give free radicals), when performed on free-radical photographic films, may produce visible images at low concentrations of the chemical agent detected.

#### K. Reaction Mechanisms.

There is a continuing interest in reaction mechanisms, since a better understanding of principles may lead to new detection schemes and an improvement of existing detection reactions.

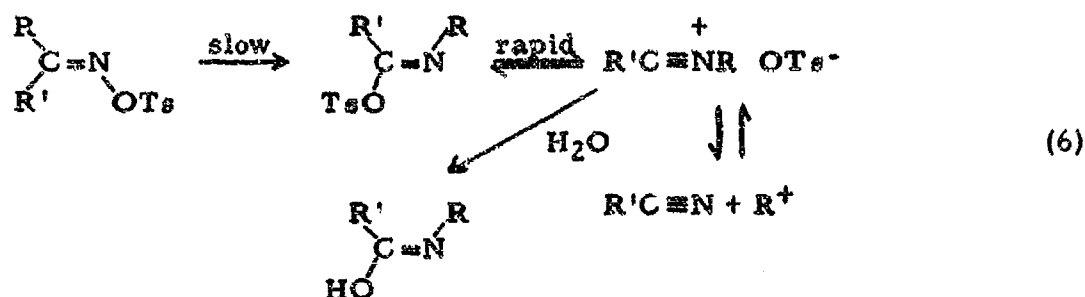
Hudson has reviewed the mechanism of phosphorylation reactions to define conditions that determine bimolecular or unimolecular hydrolysis.<sup>83</sup> Differences between chlorides and anhydrides on the one hand, and fluorides on the other, were attributed to the high P-F bond energy.

Epstein and coworkers<sup>84</sup> have studied the reactivity of isopropyl methylphosphonofluoridate with substituted phenols. The data indicate that: (1) the nucleophilic displacement capability of a phenolate increases with the basicity of the anion, (2) cationic sites in the phenol increase the reactivity of the phenolate, (3) there are marked steric effects due to ortho substituents that lower reactivity of the phenol, and (4) substances in the ortho position that are capable of hydrogen bonding can markedly increase the rate constant.

In nonhydroxylic solvents, the order of reactivity in the bimolecular acylation of phenols by chloro-substituted acyl halides decreases with increasing electron-withdrawing substitution in the acylating agent.<sup>85</sup> This is opposite to the effect found in hydroxylic media. Apparently, the relative importance of bond breaking and forming processes depends on the ability of the leaving group to depart in the medium concerned. If sufficient salt is present in the non-hydroxylic media (thus assisting in the departure of the leaving group), the order of reactivity in hydroxylic media reappears.

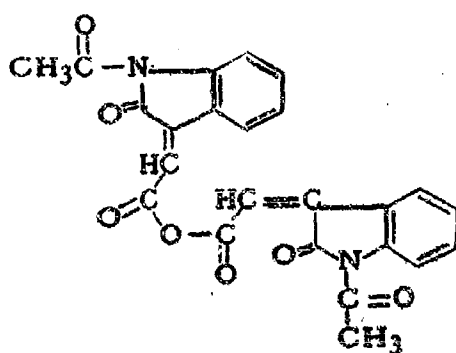
The mechanism of the Beckmann rearrangement and of the fragmentation of ketoxime tosylates has been studied by determining rate constants and products in 80% ethanol.<sup>86</sup> The ratio of fragmentation to amide formation is not related to reaction rate but increases with the stability of the carbonium

ion formed, as reflected by solvolysis rates of the corresponding alkyl chlorides. A mechanism is presented that involves a rate-determining isomerization to an imino tosylate, a rapid isomerization to a nitrilium ion, and then fragmentation or amide formation (equation 6).

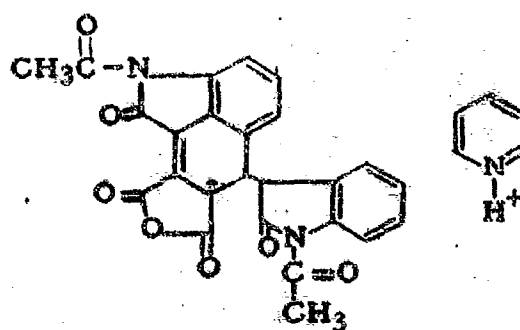


These findings do not support the classical mechanism of the Beckmann rearrangement involving alkyl migration, which assumes direct ionization rearrangement.

The condensation of isatin with acetic anhydride in the presence of pyridine yields a purple compound that is believed to be a triacetyl derivative.<sup>87</sup> A recent study indicated the compound to be XV, presumably formed from XIV, which undergoes an internal Diels-Alder reaction with subsequent rearrangement and oxidation. Compound XV absorbs only 1 mole of hydrogen to yield a yellow leuco derivative that rapidly regenerates the original salt on exposure to air.

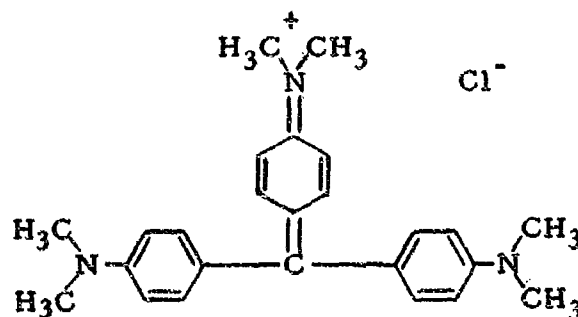


XIV



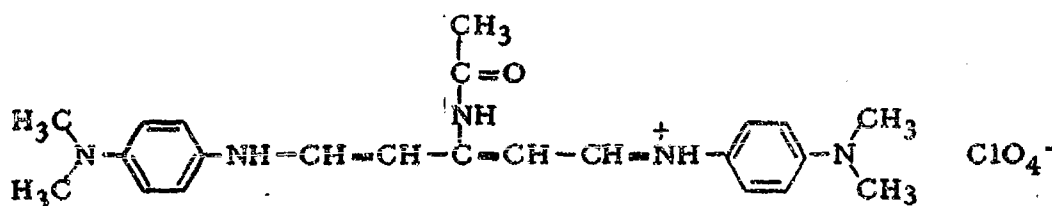
XV

Pyridine, benzoyl chloride, dimethylaminobenzene, and anhydrous cuprous chloride give Crystal Violet (XVI). Crystal Violet is usually prepared by treating a mixture of dimethyl-p-toluidine and dimethylaminobenzene with an oxidizing agent such as cupric sulfate in the presence of sodium chloride or nitrobenzene.



XVI

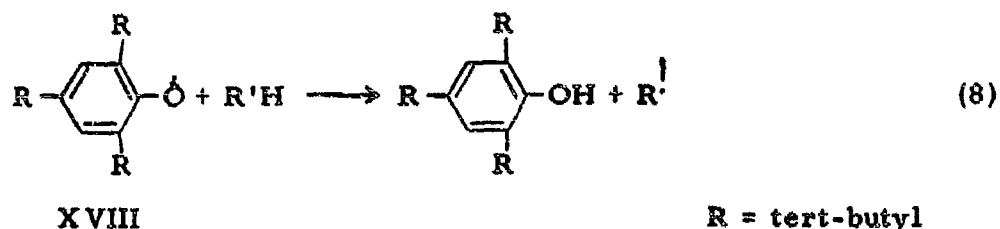
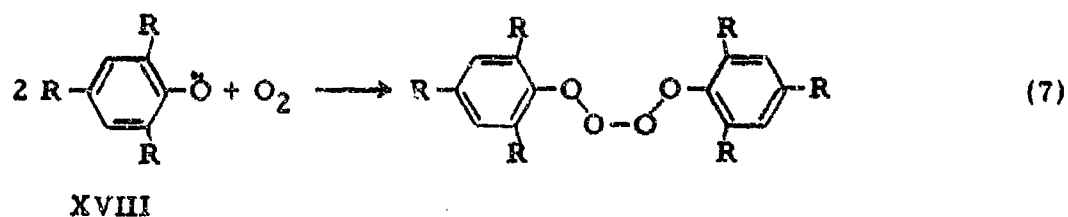
Cyanogen bromide, 4-acetamidopyridine, and p-dimethylaminoaniline in acetone-ether give a blue precipitate, which, on treatment with sodium perchlorate, gives XVII.<sup>88</sup>



XVII

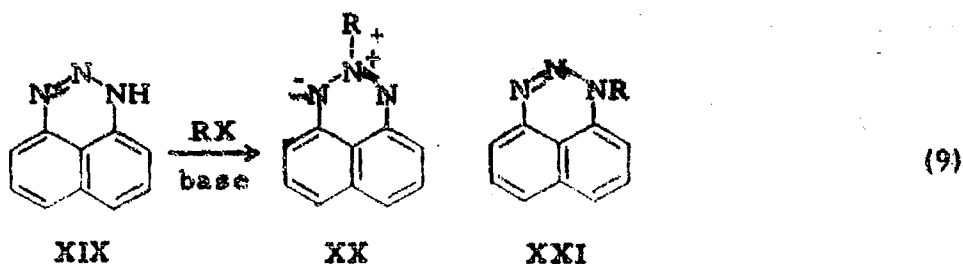
#### L. Reagents.

2, 4, 6-Tri-tert-butylphenoxyl free radical (XVIII) is a useful reagent for a quantitative determination of uncombined oxygen in organic solvents [equation (7)] and of labile hydrogen atoms in antioxidants and other oxidizable species [equation (8)].<sup>89</sup> The limit of detection is  $10^{-8}$  mole. Ferrous ion and iodide are not reactive with the radical.



N, N-Dimethyl-4-aminobiphenyl is oxidized with strong oxidizing agents to an intensely blue product and can be used as an irreversible oxidation-reduction indicator. <sup>90</sup>

The red-colored 1-H-naphtho[1,8-de]triazine (XIX) gives blue and red monomethyl derivatives (XX and XXI). The usefulness of XX as a colored product in visually observed detection reactions is limited by its low extinction coefficient (570 at 655 mμ). Nevertheless, XX represents the first member of a new class of heterocyclic compounds.



#### M. Reviews.

Several excellent reviews that may be useful to workers in detection have been published recently. <sup>91-98</sup> In particular, the review of the methods available for the detection and determination of cyanide is very complete and well done. In addition to these reviews, others may be found throughout the bibliography under specific topics of interest.

## N. Solids-Surfaces.

Solid-state reactions in which adsorption of chemical agents on surfaces initiates chain reactions are goals of current detection research. There is, however, little analogy to draw from in the design of such reactions. It is clear that understanding of the physics and chemistry of solid-state reactions is far from complete. This is particularly true of the growth and propagation of fast solid-state reactions in which the experimental difficulties inherent in such studies are great.

Solid materials that disintegrate in a chain reaction are usually in the category of explosives. There is a monograph dealing with research in this field, and, in particular, with the mechanism by which an explosive crystal can decompose.<sup>99</sup>

Explosives are also being considered as ingredients in dry photographic systems.<sup>74</sup> The materials are of two classes: (1) certain metallic azides, acetylides, and other isoelectronic compounds such as cyanates, fulminates, and thiocyanates, and (2) more complex metal-organic compounds whose dissociation can be catalyzed by metal ions.

The compounds that have been particularly successful in Robillard's investigation<sup>74</sup> are cadmium, lead, and silver azides, silver acetylide, and silver fulminate. In the metal-organic compounds, sodium bis-2,3-pentanedionodinitrocobaltate has been especially studied. A typical process involves a cuprous-ion catalysis of the dissociation of the cobalt acetyl acetonate to give cobalt as the image-forming material.

In 1964, a conference was held on surface effects in detection.<sup>100</sup> The topics discussed included fundamental factors in detecting chemicals as adsorbed films, problems in the use of surface phenomena in detection of contaminants, experiments on the specificities of human olfaction, techniques based on surface potentials and related phenomena, techniques based primarily on subsurface effects, and problems in sensitivity and specificity. It was generally agreed that a great deal of fundamental research must be performed on surface effects before exploiting the various possibilities for detection application.

Basic processes of luminescence in solids and conditions for light emission at luminescence centers have been discussed by Garlick.<sup>101</sup>

Several cells for observing the infrared spectra of molecules adsorbed on solid surfaces have been described.<sup>102</sup> Experiments with germanium oxide gel gave promise of producing a useful substrate for spectroscopic work. It has been discovered that the slow interaction between a powdered solid and an active adsorbent resulted in spectral changes that can be used for kinetic studies of the process of adsorption.<sup>103</sup>

Shcherbakova found that the capacity of silica gel for water can be decreased without changing the surface area by treating the silica with trimethylchlorosilane.<sup>104</sup>

It has been discovered that, in benzene, color reactions of acid clay with diphenylpolyenes, carotenoids, and polyacenes are due to the formation of cation radicals of these hydrocarbons in the clay.<sup>105</sup> Mixtures of aromatic azo or amino compounds in toluene or xylene and an  $\text{Al}_2\text{O}_3\text{-SiO}_2$  catalyst also give free radicals, as substantiated by esr.<sup>106</sup>

#### O. Theoretical.

Hillenbrand and coworkers dealt with some of the theoretical considerations in the microchemical detection of toxic chemical agents in the absence of concentration or sampling devices.<sup>1</sup> For the stoichiometric reaction considered, a sufficient amount of reaction to produce visible color in 10 sec in a porous solid will be possible only in regions of very high airflow velocities. Attempts to develop simple, yet sensitive, devices based on a stoichiometric reaction are impractical, and choices for catalytic reactions will be limited to those providing large effects.

The use of a computer has been described for overcoming the loss of information beyond the range of sensitivity of a given analytical method.<sup>107</sup> A programming system has also been developed for a computer search of active-site configurations.<sup>108</sup>

### III. CONCLUSIONS.

Current literature contains much information that can be used as background in attempting to solve detection problems. Detailed analysis is not the purpose of this report and is, instead, left to individual users.

A noticeable trend worth mentioning is the increasing use of free radicals as reagents, intermediates, or products in analytical reactions. Chiefly because of their rapid rates, free-radical reactions should be more closely examined for detection applications.

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